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(57) Abstract

A modified polyolefine which has good adhesion to metals and to polar substances. The polymer consists of polyolefine to which aminosilane has been added. Aminosilane has been added 0.01-10 % of the weight of the polymer.

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Modified polyolefine

The present invention concerns a modified polyolefine having good adhesion to metals and to polar substances.

Polyethylene and polyolefines in general are characterized by poor adhesion to metals and to materials containing polar groups. Somewhat better adhesion is obtained in certain instances by copolymerization of unsaturated esters, such as vinyl acetate or alkyl(meth)acrylate (methylacrylate, ethylacrylate, butylacrylate, etc.), but the adhesion also of these copolymers is insufficient in most multi-layer structures. Endeavours have been made to improve this adhesion in a number of ways. Among other things, unsaturated acids or acid anhydrides have been used as comonomer when polymerizing copolymers or terpolymers of ethylene. Examples of commercial applications are: ethylene/acrylic acid copolymer containing 9% acrylic acid, and ethylene/methacrylic acid copolymer containing 9% methacrylic acid. A commercial terpolymer known in the art contains 4% acrylic acid and 7% butylacrylate. Also commercially available is a product in which the methacrylic acid has been partially neutralized to be present as a salt, so that a so-called ionomer has been obtained. An example of the use of maleic acid anhydride towards improving adhesion is the application in which maleic acid anhydride has been grafted to LDPE, HDPE or EVA. Another example is the terpolymer of ethylene, butylacrylate and maleic acid anhydride. It is also known that the adhesion of olefines to metals and to substances containing polar groups can be improved by copolymerization or grafting of unsaturated silanes.

Although grafting with unsaturated substances may in itself be a good way to modify polyolefines in order to improve their adhesion, drawbacks may occur. Associated herewith is the fact that grafting of an unsaturated molecule to a polyolefine is based on presence of a radical former, which has the task of activating the molecule

to be grafted and to produce grafting points on the polymer chain. This comparatively complex process with its numerous non-useful side reactions, such as oligomerization or size variation of the graft branches which is caused thereby, imply eminent attentiveness in regard of the manufacturing process so that an end product might be obtained which is grafted with maximum efficiency and homogeneity.

The object of the present invention is to achieve an improvement of modified ethylene or olefine polymers known at present.

The polyolefine of the invention is mainly characterized in that it consists of a polyolefine to which has been admixed or chemically adjoined 0.01-10% substances classifiable as alkoxyaminosilanes. The silane chemically adjoined to the polyolefine may be any alkoxyaminosilane suited to this purpose. These alkoxyaminosilanes include the following: 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, and N-aminoethyl-3-aminopropyltrimethoxysilane, which shall be referred to as MEAM, EAM and DIAM, respectively, in the following.

When a polyolefine is admixed with alkoxyaminosilanes in this way, the situation is considerably more favourable than in the above-mentioned case. Therefore said additives may be adjoined either at the basic polymer synthetizing step or equally before or after it, and furthermore at the moulding step. It is thus understood that the procedure is highly flexible and affords wide possibilities as regards the quantity of substance added.

The use of aminosilanes in polyolefines is not novel in itself. Originally, hydrolyzable alkoxysilanes were developed for improving the miscibility of polymers and inorganic fillers and glass and artificial fibres (for use as so-called coupling agents). In such use, the alkoxy groups of the silane are hydrolyzed to become hydroxy groups, this being followed by condensation with hydroxyl groups on the surface of the fillers. These silanes contain, in

addition to alkoxy groups, one or several groups having a chemical composition such that they mix well with the polymer (e.g. vinyl. glycidyl, amino, mercapto, isocyanate or other reactive groups).

Since the alkoxy groups of silane are hydrolyzed and condensed by effect of water and of a catalyst, for instance dibutylstannic dilaurate, silanes have also been introduced in cross-linking techniques. This is based on the principle that an unsaturated alkoxyaminosilane is copolymerized with the polymer or chemically adjoined thereto with the aid of peroxide, cross-linking only taking place after the end product has been completed, with the aid of water or steam. Hereby it becomes possible to mould the polymer at high temperatures without risk of cross-linking; in addition, the cross-linking step is less expensive in energy as well as investment cost. When silanes are used for cross-linking, a condensation catalyst must always be present.

Silanes are also well-known as agents improving the adhesion of various glues and coatings. In applications of this kind, the silane has to be able to form strong bonds both to the matrix of the glue, or cement, substance and to the laminations which are being glued. On the other hand, the silane may have a character such that it mainly forms bonds to one given material surface, not very easily to any material flowing along the surface. Properties of this kind are required, for instance, when it is desired to prevent adhesion of a resin to the reaction vessel or to a working surface. In that case the silane serves as a so-called release substance. Adhesion-promoter or release agent properties are mainly achieved by selecting silanes on the basis of suitable chemical groups.

When, as is done in the present invention, polyolefines are modified with alkoxyaminosilanes, one starts from the above-mentioned polyolefine and 0-01-10% alkoxyaminosilane and one mixes them at a temperature at which the mix is in molten state. It is also possible to admix alkoxyaminosilane to the polyolefine at a temperature

so low, even in a dry mixing process, that it will not react until at the conversion stage.

However, on the other hand, the mixing of the invention may also be performed in one step, directly in the conversion machine, in the way that the alkoxyaminosilane is first dry-mixed with the polyolefine, whereupon the mix is melted in the initial stages of the conversion extruder at low temperature, in order to ensure complete melting of the polyolefine and uniform mixing of the alkoxyaminosilane, avoiding excessive reaction of the alkoxysilane at this stage. The temperature is only raised in the final extruder stage in order that the emerging mixture might be maximally reactive from the viewpoints of chemical bonding as well as adhesion, when it meets the substrate surface.

Alternatively, the high-content aminosilane mix of the invention may also be used by diluting it into the base plastic at the conversion stage. Said base plastic may be, but it must not necessarily be, the same plastic on which the above-mentioned high-content mixture is based.

The procedure of the invention for chemically adjoining aminosilanes to polar or non-polar polyolefines is also appropriate for ethylene homopolymers and for improving their adhesion to aluminium.

Examples of the reactions between aminosilanes and certain ethylene copolymers and homopolymers are presented in Figs 1-3.

Scrutiny of these figures reveals special features as regards the mode of reaction if the reaction mechanisms of ethylene homopolymers, alkyl, acrylate and vinylacetate copolymers are mutually compared. When aminosilane is grafted to a homopolymer, presence of moisture causes protonation of the amino group and its cleaving from the aminosilane in the form of ammonia. The remaining, positively charged silane compound then approaches, as can be seen in

Fig. 1, with the aid of the hydroxy ion a position in the negatively charged ethylene chain, and an ionic bond is formed. Thereafter, the compound begins, again, through the alkoxy groups to serve as adhesion plastic to various substrates.

Alkylacrylate copolymers react with aminosilanes through the alkoxy and/or amino groups. As can be seen in Fig. 2, the end products may on the basis hereof differ in that the branch may be connected to the polyolefine through an amide group or through an ester group. In the first case, the alkoxy groups are mediators to the other substrate, while in the latter both alkoxy and amino groups are present as mediators to form adhesion reactions to the other substrate.

Fig. 3 shows how it is possible to adjoin an aminosilane compound to an ethylene/vinylacetate copolymer through an amino or alkoxy group. As intermediate product there appears at first, bound to the chain, either a hydroxyl group or an alkoxy group, which may then with the aid of the remaining alkoxy groups of the aminosilane go through a condensation reaction so that the identical products depicted in Fig. 3 are produced. Thus, the adhesion reactions to other substances are based on reactions of the amino and silane groups.

The reaction both of alkylacrylate copolymers and of vinylacetate copolymers with aminosilanes can also be assumed to some degree to contain the mechanism reproduced in Fig. 1.

In other cases, too, in which amino groups occur for instance in an existing branch, one may expect protonation, ammonia cleaving brought about by moisture, and then as a consequence ionic coupling with the polyolefine chain (in accordance with Fig. 1).

The invention is more closely described with the aid of the examples following below.

Example 1

EBA 17 (MI = 7, BA = 17%) was extruded together with an alkoxy-aminosilane in a Brabender extruder (Ø = 19 mm, L = 20 D, and compression ratio 3:1). The silane in question, which was 3-aminopropyltrimethoxysilane, henceforward referred to as MEAM, was used in quantity 0.2-1%.

For coating aluminium and steel, a nozzle was constructed through which the metal strip (20 mm x 1.0 mm) could pe pushed. The temperature profile of the extruder was maintained such that in the three steps of the screw there was 105°C, 200°C and 250°C and finally in the nozzle, 250°C.

In this manner laminated strips were extruded (modified polyethylene copolymer and Al (or Fe)), which were tested for adhesion after 24 hrs. This test was carried out with an Instron tension tester (Peel test), the pulling rate being 50 mm/min. The force was measured after establishment of equilibrium and expressed in units N/cm.

Table I

EBA 17/Al,Fe

MEAM CONTENT	ADHESION TO METALS, N/cm	
%	Al	Fe
0	2.2	8.6
0.2	11	15
0.5	16	21
1.0	21	29

These results reveal that by admixing MEAM to EBA 17 the adhesion of EBA 17 to aluminium and steel can be improved.

Example 2

In this instance the experiment was carried out as in Example 1, except that instead of EBA 17 the ethylene/silane copolymer VISICO 1441 (MI = 4.5 and VTMO content = 1.8%) or the ethylene/silane terpolymer VISICO 1407 (MI = 5.0, VTMO content = 2.0% and butylacrylate content = 17%) was used. In this connection, VTMO means vinyltrimethoxysilane adjoined to the polymer chain in connection with polymerizing.

Table II

VISICO 1407, VISICO 1441 /Al,Fe

MEAM CONTENT %	ADHESION TO METALS, N/cm			
	Al		Fe	
	1407	1441	1407	1441
0	34	4.1	65	15
0.2	45	5.4	70	19
0.5	63	6.0	76	27
1.0	85	6.5	72	36

It is found that fair adhesion is achieved using non-modified VISICO 1407 or VISICO 1441. It is also seen that the adhesion can be even further improved by admixing MEAM aminosilane to said VISICO polymers.

Example 3

In this case the purpose was to study the comparative effect of MEAM content on the adhesion of EBA 17 to various material surfaces.

To this end, EMA 17 was first admixed with a given quantity of

MEAM (0.01-1.0%) in a Werner-Pfleiderer ZSK 30 twin screw extruder with screw diameter 30 mm and L = 38 D. The temperatures in the different extruder zones were 60, 70, 160, 170, 170, 170 and 170°C, and the production rate was 15 kg/h. The higher MEAM contents were added periodically in a Haake Rheomix 5000 mixer. Mixing temperature was 200°C and total mixing time, about 10 min. In order to obtain laminations appropriate for determinations of adhesion between modified polyethylene and another material, the mix from the mixer was pressed together with the desired materials, using a laboratory press. Pressing conditions were: temperature 180°C, pressure 50 tons, and duration 60 seconds. An epoxy surface was produced by coating a steel plate at 200°C, prior to the pressing step, with epoxy powder blown thereon. The combinations listed below consisted of two components VISICO 1441 and Hoechst PVA brand MOWIOL 4-88, which are chemically bonded end result copolymers of said materials. The results are presented in Table III.

Table III

COMPOSITION OF THE LAMINATED SURFACE	ADHESION OF EBA 17 TO THE MATERIALS LISTED, WITH VARYING MEAM CONTENT (0-10%)			
	0	0.2	1.0	- 10
PET	0	0.4	0.8	2.0
PC	0.2	0.7	1.1	1.5
EPOXY	0	1.0	1.4	1.8
PA-6	0.1	1.2	1.9	2.4
PUR	0	0.6	1.2	3.4
EVOH	0.1	0.7	2.1	2.3
VISICO 1441 (20%)/ PVA (80%) COMBINATION	0	0.4	1.1	1.7
VISICO 1441 (50%)/ PVA (50%) COMBINATION	6.3	6.6	6.8	6.9

Legend:

PET	Melinex AS	ICI
PC	Makrofol 1-1	Bayer
PUR	Desmopan 385	Bayer
EPOXY	Eurokote 714,31 (BS)	Bitumes-Speciaux
PA-6		Valke
EVOH	EVAL EP-F101	Kuraray

The results reveal that MEAM addition improves the adhesion of EBA 17 to the materials tested. Slight improvement is noted in the case of the VISICO 1441/PVA 50/50 combination, partly due to the high polyethylene proportion, wherefore non-modified EBA 17 can indeed be expected to adhere very strongly to it. It is further noted that even though the results can be somewhat improved if 10% MEAM are added, the advantages gained are neither technically nor commercially interesting.

Example 4

The purpose was in this case to institute a comparison of the adhesion of certain homopolymers and copolymers of ethylene to epoxy by detaching perpendicularly an epoxy layer coated on a steel plate, from an ethylene polymer layer coated thereupon. A steel nut fused into the ethylene polymer layer served as the other fixed point.

The specimen was prepared by spraying epoxy powder (Bitumes-Speciaux Eurokote 714,13) on a sand-blasted steel plate heated to 200°C. After a delay of 5 seconds, powdery ethylene polymer was furthermore sprayed on the epoxy, thus producing a steel plate with two plastic coatings (steel/epoxy/PE). The steel nut mentioned above was fused at 200°C into the surface layer consisting of PE homopolymer or copolymer.

The PE polymers that were tested were the polymers described before: VISICO 1407 (see Example 2), EBA 17 (see Example 1), EVA 19 (see Example 5), and B 7518 (see Example 8). They were tested in the manner described, either as such or admixing 1% MEAM to them. The results are presented in Table IV.

Table IV

	ADHESION OF CERTAIN ETHYLENE HOMOPOLYMERS AND COPOLYMERS TO EPOXY *) (BITUMES SPECIAUX EUROKOTE 714,31), AS SUCH AND AFTER MODIFICATION WITH MEAM (IN kg/cm^2)	
Polymer	0% MEAM	1.0% MEAM
VISICO 1407	49	85
EBA 17	12	63
EVA 19	14	83
B 7518	0.5	5

*) The results are based on a pulling test in which the measured values were obtained by detaching a PE/epoxy intermediate layer by perpendicular pull.

It is seen by these results that VISICO 1407 even by itself yields an effective adhesion to epoxy. Slightly poorer results are then seen in the cases of the basic polymers of EBA 17 and EVA 19, while the adhesion to epoxy of B 7518 is nearly nil. The results also indicate that the adhesions can be remarkably improved if 1% MEAM is added.

Example 5

Ethyl/vinylacetate copolymer, EVA 19 (MI = 10, VA = 19%) was extruded together with various alkoxyaminosilanes in a Brabender extruder (Ø = 19 mm, L = 20 D, and compression ratio 3:1). The abbreviation "EVA 19" is here, and subsequently, used to refer to the experimental brand NTR 223 by the company Neste Oy. The above-defined silanes, MEAM, EAM and DIAM, were used in quantities from 0,25% to 2%. The temperature profile in the extruder was 105°C, 250°C and 300°C in the different parts of the cylinder, and 300°C in the nozzle. The output was conducted into contact with the

aluminium side of a paper/Al lamination affixed to a belt web. The paper/Al lamination had 60 um thickness. The speed of travel of the web was 5 m/min, The speed of rotation of the extruder screw was 41 min^{-1}. On coming into contact with the web, the molten plastic became immediately subjected to pressure between a press roller weighing 5 kg and the web. In this manner, lamination strips (modified polymer and aluminium) were extruded, which were tested for adhesion after 24 hrs. This test was carried out in an Instron peel tester, the rate of pulling being 50 mm/min. The force was measured after reaching equilibrium, and it was expressed in units N/cm.

It is seen in Table V how the alkoxyaminosilane content (content of MEAM, EAM, DIAM) affects adhesion.

Table 5

EVA 19
Basic polymer

AMINOSILANE CONTENT, %	ADHESION TO ALUMINIUM, N/cm MEAM	DIAM	EAM
0	0.6	0.6	0.6
0.25	1.4	1.8	1.7
0.5	1.7	3.4	1.9
1.0	1.2	4.4	1.8
2.0	1.1	4.3	1.6

It is seen from these results that all alkoxyaminosilanes presented here, even at low contents, improve the adhesion to aluminium of the EVA material. It is also seen that best results are achieved by using DIAM. It may be mentioned, by way of comparison, that the adhesion of non-modified EVA 19 is 0.6 N/cm, and that results very close to zero are obtained when non-modified poly-

ethylene is used.

Example 6

In this case testing was done as in Example 5, except that instead of EVA was used the above-mentioned ethylene/butylacrylate copolymer, EBA 17 (MI = 7, BA = 17%).

Table VI

EBA 17
Basic polymer

AMINOSILANE CONTENT, %	ADHESION TO ALUMINIUM, N/cm MEAM	DIAM	EAM
0	0.3	0.3	0.3
0.2	2.6	1.8	0.6
0.5	>4.3	2.1	1.0
1.0	>4.3	3.0	3.7
2.0	4.3	2.8	1.4

From these results is now seen the adhesion-improving effect of the aminosilanes which were used, even at low contents. Best results are achieved when EBA 17 is modified with MEAM. It may be mentioned by way of comparison that the adhesion of non-modified EBA 17 is 0.3 N/cm.

Example 7

Testing was done, in this case, as in Examples 5 and 6, except that for basic plastic was now used an ethylene/methylacrylate copolymer, EMA 20 (MI = 6, MA = 20%), which is the brand EMA 2207 manufactured by Chevron.

Table VII

EMA 20
Basic polymer

AMINOSILANE CONTENT, %	ADHESION TO ALUMINIUM, N/cm MEAM	DIAM	EAM
0	0.6	0.6	0.6
0.2	1.2	1.0	1.0
0.5	2.6	1.0	2.5
1.0	2.9	1.0	2.4
2.0	2.0	0.6	1.8

These results reveal that the adhesion of EMA can also be improved by using alkoxyaminosilanes. It is however seen from the table that 20% EMA requires somewhat higher alkoxyaminosilane contents than do EVA and EBA, presented in Examples 5 and 6. Best results are obtained by using MEAM or EAM, which present equal results. It may be pointed out, by way of comparison, that the adhesion of non-modified EMA 20 is 0.6 N/cm.

Example 8

Testing was done in this case as in Examples 5-7, except that alkoxyaminosilanes were admixed to polyethylene homopolymer, LDPE (MI = 7.5, density = 0.918 g/cm^3), which represents the brand B 7518 manufactured by the company Neste Oy.

Table VIII

LDPE

Basic polymer

AMINOSILANE CONTENT, %	ADHESION TO ALUMINIUM, N/cm MEAM	DIAM	EAM
0	0	0	0
0.2	0.2	1.1	0.8
0.5	>2.4	1.7	1.0
1.0	>1.8	0.4	0.3

These results reveal that the adhesion of polyethylene homopolymer can also be improved by admixing alkoxyaminosilanes to it. They are however in general needed at somewhat higher contents, compared with those situations in which the basic plastic is a polyethylene copolymer of high comonomers. (See Tables V-VII.) Best results are obtained when MEAM is used. It may be pointed out, by way of comparison, that non-modified polyethylene homopolymer has virtually no adhesion.

Example 9

Testing was done, in this case, as in Examples 5-8, except that MEAM alkoxyaminosilane was mixed with the ethylene/silane copolymer VISICO 1407 or the terpolymer VISICO 1441, mentioned above (Example 2).

Table IX

VISICO 1407, VISICO 1441 /Al

MEAM CONTENT	ADHESION TO ALUMINIUM, N/cm	
%	1407	1441
0	1.8	1.1
0.2	2.1	1.9
0.5	3.8	2.9
1.0	4.1	3.7
2.0	3.4	3.2

We see here that both VISICO materials, 1407 and 1441, have already in themselves a considerable adhesion-improving effect, compared with other homopolymers or copolymers of ethylene. In addition, adhesion can be observed to improve further when MEAM is added. It may furthermore be noted that VISICO 1407 and MEAM mixtures based thereon yield somewhat better results than those obtained with equivalent VISICO 1441 systems.

Example 10

In this case, testing was carried out as in Examples 5-9. The purpose was to compare in EVA brands the influence of VA content on adhesion. Therefore EVA with 9% VA, which had MI 10, was also tested in addition to EVA 19. Said material, which represents the experimental brand NTR 219 of the company Neste Oy, is henceforth referred to as EVA 9. Alkoxyaminosilanes MEAM and DIAM were admixed at 0.5% and at 2%.

Table X

EVA 19, EVA 9, LDPE

VINYLACETATE CONTENT, %	ADHESION TO ALUMINIUM, N/cm	
	DIAM, %	
	0.5	2.0
0	0.7	0.4
9	1.6	2.5
19	3.4	4.3
	MEAM, %	
	0.5	2.0
0	>2.4	0.3
9	3.4	3.0
19	1,7	1,5

It is seen from these results that addition of alkoxyaminosilanes causes considerable improvement of adhesion also with EVA material having somewhat lower VA%. When MEAM was used, there was indeed an indication that adhesion becomes stronger when the VA content goes down. The above-mentioned polyethylene homopolymer LDPE (see Example 8) was used for 0% VA reference.

Example 11

The aim was in this case similar to that in Example 10, differing only in that, instead of EVA, EBA materials with various BA contents were used. The 8.5% EBA occurring in the table is a mix made by mixing in equal quantities polyethylene homopolymer LDPE (MI = 7.5) and EBA 17 (MI = 7, BA = 17%).

Table XI

EBA 17, EBA 17/LDPE 1:1, LDPE

BUTYLACRYLATE CONTENT, %	ADHESION TO ALUMINIUM, N/cm	
	MEAM, %	
	0.5	2.0
0	>2.4	0.3
8.5	3.5	3.6
17	>4.3	4.3

It is seen from the results that good adhesion can also be achieved at lower BA content. The results further show that the adhesion of MEAM-modified EBA improves with increasing BA content. The 0% BA material included as reference is the same as in Example 9.

Example 12

In this case the aim was the same as in Examples 19 and 11, except that now a comparison was instituted concerning the effect of MA content on the adhesion of EMA copolymers when MEAM has been admixed to said copolymer. The 10% EMA appearing in Table XII was obtained by admixing EMA 20 with the above-mentioned LDPE polyethylene homopolymer.

Table XII

EMA 20, EMA 20/LDPE 1:1, LDPE

METHYLACRYLATE CONTENT, %	ADHESION TO ALUMINIUM, N/cm	
	MEAM, %	
	0.5	2.0
0	2.4	0.3
10	5.3	2.2
20	2.6	2.9

It is seen from the results that when 0.5% MEAM are admixed rather good adhesion is obtained. When higher silane content is used (2%), improvement of adhesion is observed with increasing methylacrylate content. The better adhesion with 0.5% MEAM in the case of 10% EMA, compared with EMA 20, is likely to be due to more uniform distribution of MEAM along the polymer chain. The reference 0% MA material is the same as in Examples 10 and 11.

Example 13

In this case, testing was done with reference to aluminium adhesion as in Examples 5-12. Comparisons were also made regarding adhesion to other materials (Polyamide-6, BASF Ultramid B4; ethylenevinylalcohol (EVOH), EVAL-F; steel). For steel coating a nozzle was developed through which a metal strip (20 mm x 1.0 mm) could be pushed. The temperature profile in the extruder was then: in the cylinder 105°C, 200°C and 250°C, and in the nozzle 250°C, except in the extrusion of EVOH, in which the temperatures of the nozzle and of the zone preceding same were 220°C and 200°C. When extruding EVOH and PA-6 conditions were the same otherwise, except that a nozzle of coextrusion type was used. EVA 19 (MI = 10, VA = 19%) or EVA 9 (MI = 10, VA = 9%), or EBA 17 (MI = 7, BA = 17%) or

EMA 20 (MI = 6, MA = 20%) were admixed with 0.2, 0.5, 1.0 and 2.0% MEAM. Table XIII reveals how said modified polymers and their basic polymers adhere to various materials.

Table XIII

POLYMER/% MEAM	ADHESION TO VARIOUS SUBSTRATES, N/cm			
	PA-6	EVOH	Al	Fe
EBA 17/0	0.8	0.4	0.3	22
/0.2	1.1	0.8	2.1	27
/0.5	1.8	1.2	>4.3	32
/1.0	1.3	3.3	>4.3	21
/2.0	1.2	1.6	4.3	20
EVA 19/0	1.5	0.3	0.6	28
/0.2	78	42	1.4	41
/0.5	42	39	1.7	70
/1.0	50	39	1.2	65
/2.0	45	35	1.3	62
EVA 9/0	0.1	0.1	0	11
/0.2	2.9	3.1	1.8	20
/0.5	7.5	7.4	3.4	45
/1.0	8.3	7.8	3.3	26
/2.0	6.2	7.5	3.0	35
EMA 20/0	1.0	0.2	0.6	23
/0.2	18	0.7	1.6	25
/0.5	37	1.2	2.6	28
/1.0	40	0.3	2.9	21
/2.0	38	0.9	2.0	22

It is once again seen from these results, in summary, that EBA 17, EVA 9, EVA 19 and EMA 20 have some adhesion to aluminium, but considerable improvement is gained by admixing MEAM to them. Best adhesions are achieved when EBA 17 is used for basic polymer and somewhat poorer adhesions, using EVA 9. There is no appreciable change of adhesion values when the silane content is raised from 0.5 to 2.0%.

When MEAM is admixed to the above-mentioned basic polymers, improvement of adhesion to steel is also achieved, compared with the basic polymer. When the silane content is increased from 0.5 to 2.0%, the adhesions are unchanged or fall at high content. Best adhesions to steel are obtained when using EVA 19 for basic polymer.

It is also noted that the adhesion of the above-mentioned basic polymers to ethylenevinylalcohol (EVOH), as well as to polyamide (PA-6), can be considerably improved by admixing MEAM to them. Rather good results are noted on the PA-6 side with EVA 19 or EMA 20 for basic plastic, and regarding EVOH when EVA 19 is used.

Example 14

In this case the testing was done as in the preceding Example, except that comparisons were made for commercial adhesion plastics.

Table XIV shows the manner in which MEAM-modified EBA, EVA and EMA adhere to various materials, compared with commercial adhesion plastics.

Table XIV

POLYMER	ADHESION, COMPARED TO COMMERCIAL PRODUCTS, N/cm			
	PA-6	EVOH	Al	Fe
EBA 17 + 0.5% MEAM	1.8	1.2	>4.3	32
EBA 17 + 1.0% MEAM	1.3	3.3	>4.3	21
EVA 19 + 0.5% MEAM	42	39	1.7	70
EVA 19 + 1.0% MEAM	50	39	1.2	65
EMA 20 + 0.5% MEAM	37	1.2	2.6	28
EMA 20 + 1.0% MEAM	40	0.3	2.9	21
PRIMACOR 1420 9% AA	55	2.6	1.9	63
NUCREL 0903 9% MAA	23	1.3	0.7	59
SURLYN 1652 12% MAA + ZN	26	0.1	1.0	36
CXA 3095	7.0	3.4	1.5	10
LUPOLEN A 2910 M 4% AA + 7% BA	37	3.4	1.5	69

These results reveal that for instance with MEAM-grafted EBA, EMA and EVA in many instances equally good or better adhesion, compared with competing products, has been obtained to polyamide, ethylenevinylalcohol, aluminium and steel.

Claims

1. A modified polyolefine with good adhesion to metals and polar substances, **characterized** in that it consists of polyolefine to which aminosilane has been added.

2. Polyolefine according to claim 1, **characterized** in that aminosilane has been added 0.01-10% of the weight of polyolefine.

3. Polyolefine according to claim 1 or 2, **characterized** in that the aminosilane has been chemically adjoined to the polyolefine.

4. Polyolefine according to any one of claims 1-3, **characterized** in that the polyolefine is polyethylene (LDPE, VLDPE, LLDPE, MDPE or HDPE), an ethylene copolymer, a grafted copolymer or a mixture of ethylene polymer.

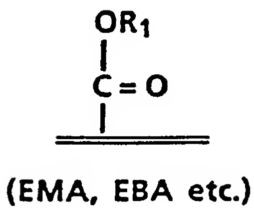
5. A multi-layered plastic product with good adhesion between layers, **characterized** in that it consists of at least one layer which has been manufactured of a polyolefine according to any one of claims 1-4 and of one or several layers consisting of a metal, a polar substance, and possibly of one or several non-modified polyolefine layers.

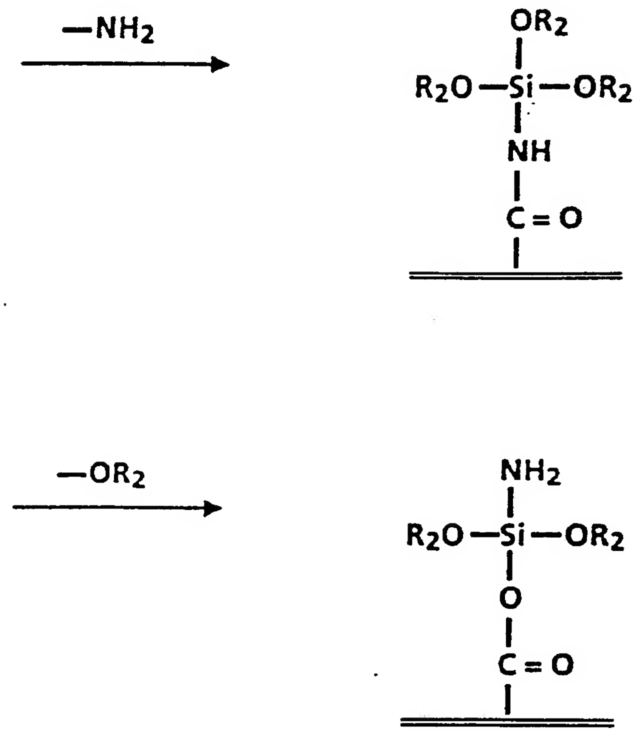
6. Multi-layered product according to claim 5, **characterized** in that it is a multi-layer film, a multi-layer tube, a multi-layer bottle or a multi-layer shielding material occurring in a cable.

7. Multi-layered product according to claim 5, **characterized** in that the metal layers consist of steel, aluminium, and the polar plastic layers consist of polyamide, polyester, epoxy, polyurethane, polycarbonate, EVOH or a combination polymer of polyolefine and PVA.

8. Procedure for manufacturing a multi-layered product according to claim 5, **characterized** in that aminosilane has been added in the polyolefine synthesis step (before or after the reactor), at a separate compounding step, or in conjunction with extrusion of the final product.

THE MECHANISM OF THE COUPLING REACTION BETWEEN AMINOALKOXYSILANE AND A CONVENTIONAL P E COPOLYMER



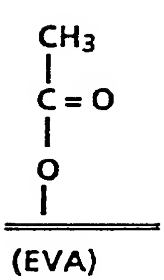


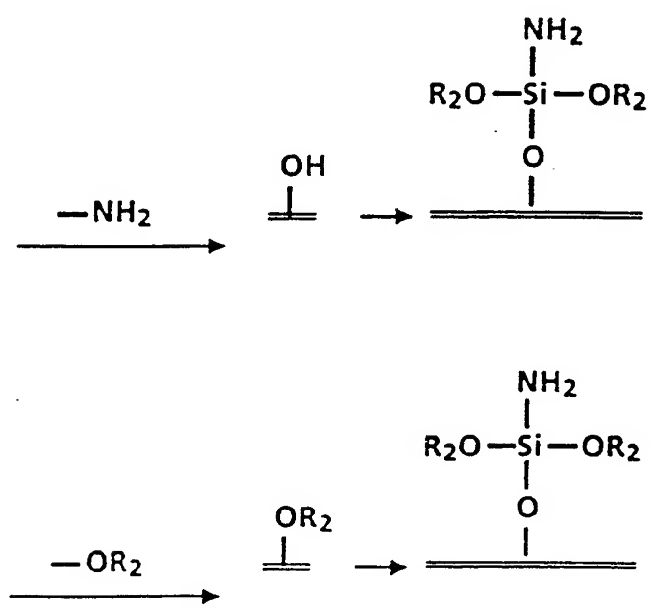
I

II

FIG. 1

FIG. 2





III

III

POSSIBLE MECHANISM OF THE REACTION BETWEEN POLYETHYLENE AND AMINOSILANE

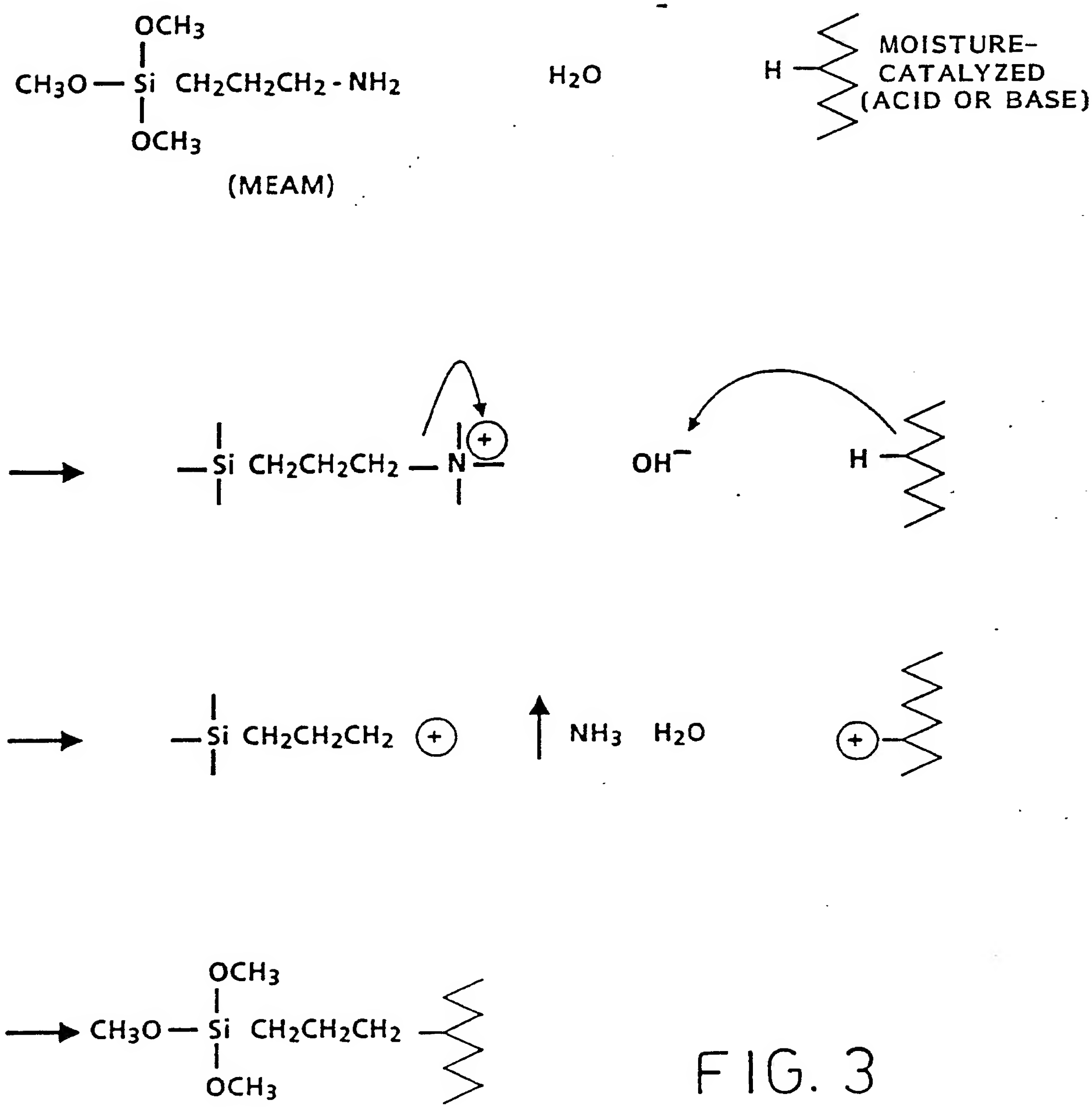


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI88/00004

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC 4

C 08 L 23/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC 4	C 08 F 8/30; C 08 J 5/12; C 08 K 5/54; C 08 L 23/00 - /08 .../...

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	EP, A1, 0 003 239 (UNION CARBIDE CORPORATION) 8 August 1979 & JP, 54129042 CA, 1106165 AU, 524407	1-8
X	EP, A2, 0 023 239 (UNION CARBIDE CORPORATION) 4 February 1981 & JP, 56022003 US, 4263158 AT, 374298	1-8
X	EP, A1, 0 053 022 (EXXON RESEARCH AND ENGINEERING COMPANY) 2 June 1982 & GB, 2088387 JP, 57123250 US, 4463129 AT, E, 8654	1-8
X	EP, A1, 0 075 956 (UNION CARBIDE CORPORATION) 6 April 1983 .../...	1-8

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1988-04-05	1988 -04- 12
International Searching Authority	**Signature of Authorized Officer**
Swedish Patent Office	Jack Hedlund Jack Hedlund

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

II Fields searched (cont)

US Cl 523: 202, 212, 213;
524: 261-269, 536, 585-587

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter not required to be searched by this Authority, namely:

2.☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3.☐ Claim numbers.........., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.